

Syntheses and characterisation of ruthenium carbonyl clusters containing phosphorus and arsenic bridging ligands

K NATARAJAN* and G HUTTNER†

Department of Chemistry, Bharathiar University, Coimbatore 641 046, India

†Fakultät für Chemie der Universität Konstanz, D 7750 Konstanz W. Germany

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Abstract. Ruthenium carbonyl clusters, $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$, $[\text{Ru}_4(\text{CO})_{12}(\mu_3\text{-AsC}_6\text{H}_5)_2]$ and $[\text{Ru}_5(\text{CO})_{16}(\mu_3\text{-P}(\text{C}_6\text{H}_5)_2)_2]$ have been synthesised and characterised by elemental analysis, NMR (^1H and ^{31}P), mass and infrared spectral measurements. Structures have been proposed on the basis of the spectroscopic data.

Keywords. Ruthenium carbonyl cluster; phosphorus and arsenic ligands.

1. Introduction

Considerable amount of work has been done on homo and heterometallic carbonyl clusters containing $\mu_3\text{-PR}$ bridged ligands (Huttner *et al* 1976b, c, 1978a, b; De 1979). Comparatively very little attention has been paid to the analogous $\mu_3\text{-AsR}$ bridged clusters and only a few are reported Huttner *et al* 1976a; Rottinger and Vahrenkamp 1978; Schneider and (Huttner 1981; Natarajan *et al* 1981). Our interest in the reactivity of clusters stabilised by bridging or capping arsenic ligands (Natarajan *et al* 1981) has led us to attempt the preparation of ruthenium chromium heterometallic cluster from $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ and $\text{Ru}_3(\text{CO})_{12}$. The reactions of primary phosphines PRH_2 (R = alkyl or aryl) with $\text{M}_3(\text{CO})_{12}$ (M = Fe, Ru) (Huttner *et al* 1980; Natarajan *et al* 1981) yielded $[(\mu_3\text{-H})_2\text{M}_3(\text{CO})_9(\mu_3\text{-PR})]$ and $(\text{M}_3(\text{CO})_9(\mu_3\text{-PR})_2]$ whereas with osmium, the mono-substituted $[\text{Os}_3(\text{CO})_{11}(\text{PRH}_2)]$ and edge bridged $[(\mu_3\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_2\text{-PRH})]$ have been obtained (Natarajan *et al* 1981a). It is quite possible that the reactions of PRH_2 with $\text{M}_3(\text{CO})_{12}$ (M = Fe, Ru) also occur with initial substitution of a CO group in $\text{M}_3(\text{CO})_{12}$ by primary phosphines leading to $[\text{M}_3(\text{CO})_{11}(\text{PRH}_2)]$, with subsequent migration and CO substitution process, resulting in $[(\mu_2\text{-H})\text{M}_3(\text{CO})_{10}(\mu_3\text{-PRH})]$ and $[(\mu_2\text{-H})\text{M}_3(\text{CO})_9(\mu_3\text{-PR})]$. Though we have been unsuccessful in obtaining the intermediates in our attempts, a recent paper (Iwasaki *et al* 1981) describes the isolation of the intermediate

* To whom all correspondence should be made

$[(\mu_2\text{-H})\text{Ru}_2(\text{CO})_{10}(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2\text{H})]$. Hence, we carried out the reaction of secondary phosphine, $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ with $\text{Ru}_3(\text{CO})_{12}$ with a view to obtaining the edge bridged cluster $[(\mu_2\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)]$, since the secondary phosphine would prevent the formation of capped cluster and favour only the edge bridged one. This paper reports the results on the reactions of $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ and $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ with $\text{Ru}_3(\text{CO})_{12}$.

2. Experimental

2.1. Materials and characterisation

Dodecacarbonyltriruthenium (Bruce and Stone 1967) and $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ (Strohmeier 1964) were prepared according to the published methods. $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ was obtained from Strem chemical corporation. The solvents used were dried over sodium-benzophenone and distilled under nitrogen. All operations were performed either under oxygen free nitrogen or under vacuum. Microanalyses were done at the Microanalytical section of the Department of Chemistry, University of Constance, W. Germany. Infrared spectra were obtained on a Zeiss IR spectrometer IMR-40 and NMR (^{31}P and ^1H) were recorded on Bruker WP-80 FT spectrometer. Mass spectra were obtained with a Varian MAT 312 spectrometer at 70 eV. Melting points were determined in open capillaries using Gallenkamp melting point apparatus and are uncorrected.

2.2. Preparations

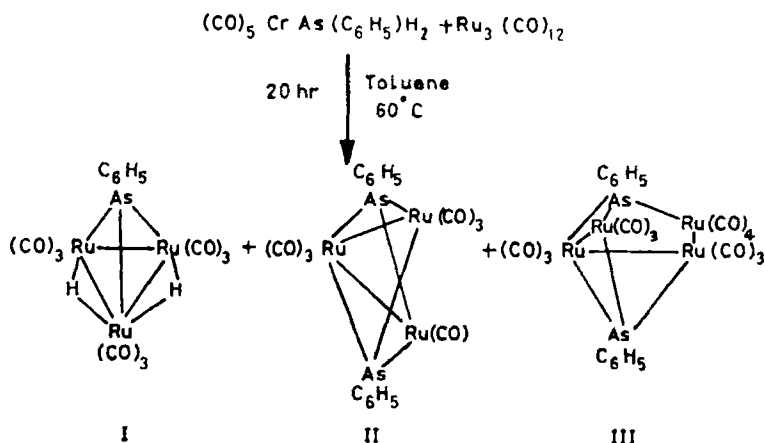
2.2a. Reaction of $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ with $\text{Ru}_3(\text{CO})_{12}$: To a suspension of $\text{Ru}_3(\text{CO})_{12}$ (320 mg, 0.5 mmol) in toluene (60 cm³) was added $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ (173 mg, 0.5 mmol) and stirred at 60° C for 20 hr. The solvent was evaporated under vacuum to a small volume (5 cm³) and silica gel (5 g) was added to it. The residue was then dried under vacuum and transferred to a silica gel column made up of pentane at -30° C. The first, yellow fraction, eluted with pentane gave $\text{Ru}_3(\text{CO})_{12}$. The second, yellow fraction, eluted with 10/1 pentane/toluene, gave $[(\mu_2\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (45 mg, 12.6% based on $\text{Ru}_3(\text{CO})_{12}$). The third, red fraction, eluted with 2/1 pentane/toluene, gave $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (38 mg, 8.8% based on $\text{Ru}_3(\text{CO})_{12}$). The fourth, red fraction eluted with 1/1 pentane/toluene gave $[\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (26 mg, 5% based on $\text{Ru}_3(\text{CO})_{12}$). $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ m.p. 140-44° C (d). Mass spec. m/e 859. Anal. Calcd. for $\text{C}_{21}\text{H}_{10}\text{O}_9\text{As}_2\text{Ru}_3$: C, 29.33; H, 1.16; As, 17.46. Found: C, 29.76; H, 1.12; As, 17.82%. IR (toluene): 2115 (s); 2083 (s); 2058 (s); 2019 (m); 1997 (w); 1926 (s) cm⁻¹. $^1\text{H-NMR}$ (Acetone-d₆): 7.55 (m) ppm. $[\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsC}_6\text{H}_5)_2]$: m.p. 165-170° C (d). Mass. spec. m/e 1072. Anal. Calcd. for $\text{C}_{25}\text{H}_{10}\text{O}_{13}\text{As}_2\text{Ru}_4$: C, 27.98; H, 0.93; As, 13.99. Found: C, 28.10; H, 0.88, As, 14.21. IR (toluene): 2140 (w); 2070 (s); 2054 (s); 2035 (m); 2025 (w); 2015 (w); 1937 (m); 1983 (w). $^1\text{H-NMR}$ (acetone-d₆): 7.32 (m) ppm.

2.2b. Reaction of $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ with $\text{Ru}_3(\text{CO})_{12}$: To a suspension of $\text{Ru}_3(\text{CO})_{12}$ (320 mg, 0.5 mmol) in toluene (60 cm³) was added $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ (93 mg, 0.5 mmol) and stirred at 60° C for 12 hr. The product, after work up as given

under §2.2a, was separated by chromatography. The first yellow fraction, eluted with 10/1 pentane/toluene gave $\text{Ru}_3(\text{CO})_{11}$. The second, yellow fraction, eluted with 2/1 pentane/toluene gave $[\text{Ru}_2(\text{CO})_6(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)_2]$ (32 mg, 8.6% based on $\text{Ru}_3(\text{CO})_{12}$). m.p. 140–45° C (d) mass. spec. m/e 740. Anal. calcd. for $\text{C}_{30}\text{H}_{20}\text{O}_6\text{P}_2\text{Ru}_2$: C, 48.65; H, 2.70; P, 8.38. Found: C, 48.96; H, 2.82; P, 8.38. IR (toluene): 2078 (s); 2044 (s); 2027 (s); 1985 (m); 1971 (w) cm^{-1} . ^{31}P NMR (toluene): 163.1 (s) ppm. ^1H -NMR (acetone- d_6): 7.55 (m) ppm.

3. Results and discussion

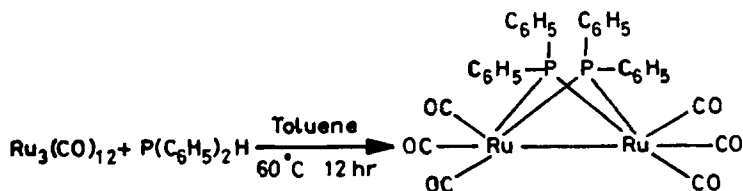
One of the methods for the synthesis of heterometallic phosphorus-bridged clusters involves in dehalogenation of dichlorophosphine complexes by iron carbonyl, $\text{Fe}_3(\text{CO})_{12}$ (Huttner *et al* 1976b, c, 1978a, b; De 1979). However, $\text{Ru}_3(\text{CO})_{12}$ did not function like $\text{Fe}_3(\text{CO})_{12}$ and yielded only homometallic clusters of the type $[\text{Ru}_5(\text{CO})_{15}(\mu_4\text{-PR})]$ (Natarajan *et al* 1981b). But, $[(\text{C}_5\text{H}_5)(\text{CO})_2\text{MnPRH}_2]$ reacts with $\text{Ru}_3(\text{CO})_{12}$ to give the expected heterometallic cluster $(\text{RPMnRu}_2(\text{CO})_8(\text{C}_5\text{H}_5))$ (Schneider and Huttner 1981). In the present study, we extended this method in order to obtain the corresponding arsenic bridged heterometallic cluster. Surprisingly, from the reaction of $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ with $\text{Ru}_3(\text{CO})_{12}$, we did not obtain the expected heteronuclear cluster of the type, $[\text{C}_6\text{H}_5\text{AsCrRu}_2(\text{CO})_{11}]$ but isolated chromium free $[(\mu_2\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$, $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ and $(\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsC}_6\text{H}_5)_2)$. The fate of the chromium fragment is not clear at present, nor is the role played by chromium in this reaction



The compound $[(\mu_2\text{-H})_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (I) has already been reported (Natarajan *et al* 1981). Mass spectroscopic and analytical data indicate that the cluster II has the composition $[\text{Ru}_3(\text{CO})_9(\text{AsC}_6\text{H}_5)_2]$. The molecular peak in the mass spectrum for this compound was quite apparent and fragmentation by successive loss up to 9 carbonyl groups has been observed. IR spectrum is very similar to the one observed for the analogous $(\text{Fe}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2)$ (Huttner *et al* 1976a) indicating a similar structure. In the ^1H -NMR spectrum, a multiplet around 7.55 ppm shows the presence of phenyl groups. Based on the spectro-

scopic data and in comparison with the known crystal structure of $[\text{Fe}_3(\text{CO})_9(\mu_3\text{-AsC}_6\text{H}_5)_2]$, structure II has been proposed.

Along with compounds I and II, a third compound $[\text{Ru}_4(\text{CO})_{13}(\mu_3\text{-AsC}_6\text{H}_5)_2]$ (III) has also been obtained from the reaction of $[(\text{CO})_5\text{CrAs}(\text{C}_6\text{H}_5)_2\text{H}_2]$ with $\text{Ru}_3(\text{CO})_{12}$. Analytical and mass spectroscopic data confirm the molecular formula $[\text{Ru}_4(\text{CO})_{13}(\text{AsC}_6\text{H}_5)_2]$. Non equivalent nature of the carbonyl groups is apparent from the more number of infrared bands observed in the ν_{CO} region (refer experimental section). The presence of phenyl groups is inferred from the $^1\text{H-NMR}$ spectrum of this compound which shows a resonance at 7.32 (m) ppm. The crystal and molecular structure has been determined by single crystal x-ray diffraction technique (Natarajan *et al* 1982) which is as shown in III.



The reaction of $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ with $\text{Ru}_3(\text{CO})_{12}$ yielded $[\text{Ru}_2(\text{CO})_6(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)_2]$. The pattern of $\nu_{(\text{CO})}$ bands observed in the infrared spectrum of this compound is close to that observed for the analogous compounds $[\text{Fe}_2(\text{CO})_8(\text{PRH})_2]$ (Treichel *et al* 1972), $[\text{Ru}_2(\text{CO})_6(\text{AsMe}_2)_2]$ (Roland and Vahrenkamp 1980) and $[\text{Ru}_2(\text{CO})_6(\text{As}(\text{C}_6\text{H}_5)_2\text{H})_2]$ (Natarajan *et al* 1981) which shows that the framework geometry is similar to the one found for these compounds with a nonplanar Ru_2P_2 cycle. Its $^{31}\text{P-NMR}$ spectrum shows a singlet at 163.1 ppm which indicates chemically equivalent bridging phosphorus ligands. In the $^1\text{H-NMR}$ spectrum a multiplet at 7.55 ppm indicates the phenyl groups.

The reaction of $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ with $\text{Ru}_3(\text{CO})_{12}$ has been carried out with the view to obtaining edge bridged hybrid cluster $[(\mu_2\text{-H})\text{Ru}_3(\text{CO})_{10}(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)_2]$ analogous to the osmium cluster $[(\mu_2\text{-H})\text{Os}_3(\text{CO})_{10}(\mu_2\text{-PRH})]$ (Natarajan *et al* 1981a). It is anticipated that the secondary phosphine, $\text{P}(\text{C}_6\text{H}_5)_2\text{H}$ would prevent the formation of capped cluster and would favour only the edge bridged one. However, we could only isolate a bridged dinuclear compound, $[\text{Ru}_2(\text{CO})_6(\mu_2\text{-P}(\text{C}_6\text{H}_5)_2)_2]$. It could be that the conditions necessary for the formation of edge bridged cluster will at the same time promote the rupture of M-M bond leading to the dinuclear species with subsequent formation of an additional phosphorus bridge.

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References

- Bruce M I and Stone F G A 1967 *J. Chem. Soc.* A 1238
De R L, Seyerl J V and Huttner G 1979 *J. Organometal. Chem.* 178 319

- Field J S, Haines T J, Smit D N, Natarajan K, Scheidsteger O and Huttner G 1982 *J. Organometal. Chem.* **246** C23
- Huttner G, Mohr G, Frank A and Seyerl J V 1976a *J. Organometal. Chem.* **118** C73
- Huttner G, Mohr G and Frank A 1976b *Angew. Chem.* **88** 719
- Huttner G, Frank A and Mohr G 1976c *Z. Naturforsch.* **B31** 1161
- Huttner G, Mohr G, Friedrich P and Schmid H G 1978a *J. Organometal. Chem.* **160** 59
- Huttner G, Mohr G and Friedrich P 1978b *Z. Naturforsch.* **B33** 1254
- Huttner G, Schneider J, Muller H D, Mohr G, Seyerl J V and Wohlfahrt L 1979 *Angew. Chem.* **91** 82
- Huttner G, Schneider J, Mohr G and Seyerl J V 1980 *J. Organometal. Chem.* **191** 161
- Iwasaki F, Mays M J, Raithby P R, Taylor P L and Wheatley P J 1981 *J. Organometal. Chem.* **213** 185
- Natarajan K, Scheidsteger O and Huttner G 1981 *J. Organometal. Chem.* **221** 301
- Natarajan K, Zsolnai L and Huttner G 1981a *J. Organometal. Chem.* **220** 365
- Natarajan K, Zsolnai L and Huttner G 1981b *J. Organometal. Chem.* **209** 85
- Roland E and Vahrenkamp H 1980 *Chem. Ber.* **113** 1799
- Rottinger E and Vahrenkamp H 1978 *Angew. Chem.* **90** 294
- Schneider J and Huttner G 1981 Unpublished results
- Strohmeier 1964 *Angew. Chem.* **76** 873
- Trischel P M, Dean W K and Douglas W M 1972 *Inorg. Chem.* **11** 1609